(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 193 305 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
03.04.2002 Bulletin 2002/14

(51) Int Cl.[7]: **C09K 5/04**

(21) Application number: **00310474.2**

(22) Date of filing: **24.11.2000**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **27.09.2000 US 670738**

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(54) Hydrofluorocarbon refrigerant compositions soluble in lubricating oil

(57) Hydrofluorocarbon refrigerants are not soluble in hydrocarbon oil. Retrofitting refrigeration equipment with hydrofluorocarbons generally entails the use of expensive polyol ester (POE) lubricants. The invention provides hydrofluorocarbon refrigerant compositions that are soluble in hydrocarbon oil thus allowing for a simpler and less expensive retrofit option to the refrigerant user.

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Description

Field of the Invention

[0001] The invention relates generally to compositions for use as refrigerants, aerosol propellants, heat transfer media, gaseous dielectrics, fire-extinguishing agents, foam blowing agents and solvents. More particularly, the invention relates to hydrofluorocarbon refrigerant compositions that are soluble in lubricating oil.

Background of the Invention

[0002] Fluorocarbon based fluids have found widespread use in industry for refrigeration, air conditioning and heat pump applications.

[0003] Vapor compression cycles are one common form of refrigeration. In its simplest form, the vapor compression cycle involves changing the refrigerant from the liquid to the vapor phase through heat absorption at a low pressure, and then from the vapor to the liquid phase through heat removal at an elevated pressure.

[0004] While the primary purpose of refrigeration is to remove energy at low temperature, the primary purpose of a heat pump is to add energy at higher temperature. Heat pumps are considered reverse cycle systems because for heating, the operation of the condenser is inter-changed with that of the refrigeration evaporator.

[0005] The art is continually seeking new fluorocarbon based fluids, which offer alternatives for refrigeration and heat pump applications. Currently, of particular interest, are fluorocarbon-based mixtures, which are considered to be environmentally acceptable substitutes for the presently used chlorofluorocarbons. The latter, such as monochlorodifluoromethane (R-22) are suspected of causing environmental problems in connection with the earth's protective ozone layer.

[0006] The substitute materials must also possess those properties unique to the chlorofluorocarbons including similar refrigeration characteristics, chemical stability, low toxicity, non-flammability, efficiency in-use and low temperature glides.

[0007] By "similar refrigeration characteristics" is meant a vapor pressure that is plus or minus 20 percent of the reference refrigerant at the same temperature.

[0008] The characteristic of efficiency in-use is important, for example, in air conditioning and refrigeration where a loss in refrigerant thermodynamic performance or energy efficiency may have secondary environmental impacts through increased fossil fuel usage arising from an increased demand for electrical energy.

[0009] Alternative hydrofluorocarbon refrigerants are known. R-507 is an azeotrope-like blend of pentafluoroethane (R-125) and 1,1,1-trifluoroethane (R-143a). R-404A is a non-azeotropic blend of R-125, R-143a and 1,1,1,2-tetrafluoroethane (R-134a). R-407 is a non-azeotropic blend of difluoromethane (R-32), R-125 and R-134a. These alternative refrigerants are available commercially from various sources including Honeywell, DuPont, Atochem and ICI.

[0010] R-407C serves as a non-ozone-depleting replacement for R-22 in various air-conditioning applications, as well as in most refrigeration systems including chillers. Since R-407C is a close match to R-22 it also serves as a retrofit fluid in applications where R-22 is generally used.

[0011] The widespread commercial use of chlorine-free hydrofluorocarbon refrigerants has been hindered, however, by the lack of commercially adequate lubricants. Mineral oil or alkyl benzenes, which have been used traditionally with R-22, are immiscible with R-407C and must therefore be replaced with expensive polyol ester lubricants. In retrofitting refrigerant systems with hydrofluorocarbon refrigerants it is necessary to drain as much of the oil as possible before adding the replacement lubricant. Often this entails removing the compressor from the system to drain lubricant. A chlorine-free R-22 retrofit fluid that is soluble in lubricating oils would advance the art.

Summary of the Invention

[0012] The invention provides refrigerant compositions that are soluble in lubricating oils and are particularly useful as R-22 retrofit fluids.

[0013] The compositions of the invention comprise a refrigerant and a solubilizing agent. Preferably the refrigerant is a hydrofluorocarbon refrigerant. Optionally, the compositions of the invention further comprise a lubricating oil selected from the group consisting of mineral or hydrocarbon oil, alkyl benzene oil, white or paraffinic oil and mixtures thereof.

[0014] In one embodiment of the invention, there is provided a composition comprising a refrigerant selected from the group consisting of the compounds listed in Table I and mixtures thereof and at least one solubilizing agent selected from the group consisting of the compounds listed in Table II and mixtures thereof.

[0015] In another embodiment, there is provided a composition comprising (i) from about 80 to about 99.9 weight percent, preferably from about 90 to about 99.9 weight percent, of a refrigerant selected from the compounds listed in

Table I and mixtures thereof; and (ii) from about 20 to about 0.1 weight percent, preferably from about 10 to about 0.1 weight percent, of a solubilizing agent selected from the compounds listed in Table II and mixtures thereof.

[0016] In yet another embodiment of the invention, there is provided a composition comprising (i) from about 80 to about 99.9 weight percent, preferably from about 90 to about 99.9 weight percent, of a refrigerant selected from Table III; and (ii) from about 20 to about 0.1 weight percent, preferably from about 10 to about 0.1 weight percent, of a solubilizing agent selected from the compounds listed in Table II and mixtures thereof.

[0017] In still another preferred embodiment, there is provided a composition comprising (i) from about 80 to about 99.9 weight percent, preferably from about 90 to about 99.9 weight percent, of a refrigerant selected from Table IV; and (ii) from about 20 to about 0.1 weight percent, preferably from about 10 to about 0.1 weight percent, of a solubilizing agent selected from the compounds listed in Table II and mixtures thereof.

[0018] In a particularly preferred embodiment, there is provided a composition comprising (i) from about 80 to about 99.9 weight percent, preferably from about 90 to about 99.9 weight percent, of a refrigerant selected from the group consisting of R-407C, R-410A, R-404A and R-507A; and (ii) from about 20 to about 0.1 weight percent, preferably from about 10 to about 0.1 weight percent, of a solubilizing agent selected from the group consisting of butane, isobutane, pentane, dimethyl ether, and mixtures thereof.

[0019] When a lubricating oil is present, it is present in an amount of from about 1 to about 60 weight percent, preferably from about 10 to about 50 weight percent, based on the total composition.

[0020] In a process embodiment, there is provided a method for producing refrigeration which comprises condensing a composition of the invention and thereafter evaporating the composition in the vicinity of a body to be cooled.

[0021] In another process embodiment, there is provided a method for producing heating which comprises condensing a composition of the invention in the vicinity of a body to be heated and thereafter evaporating the composition.

Detailed Description of the Invention and Preferred Embodiments

[0022] The refrigerant may comprise any one of the compounds listed in Table I or mixtures thereof. Hydrofluorocarbon refrigerants are preferred. The term hydrofluorocarbon refers to compounds composed solely of carbon, hydrogen and fluorine atoms. Of the hydrofluorocarbon refrigerants listed in Table I, R-32, R-143a, R-125, R-134a and mixtures thereof are preferred.

[0023] Refrigerant mixtures are preferred. Representative refrigerant mixtures are listed in Table III. Hydrofluorocarbon refrigerant mixtures are preferred. Of the hydrofluorocarbon refrigerant mixtures listed in Table III, R-404A, R-407C, R-410A and R-507A are preferred. Hydrofluorocarbon refrigerant mixtures selected from Table IV are also preferred.

[0024] As used herein, the term solubilizing agent refers to a compound that increases the solubility of a hydrofluorocarbon refrigerant and a lubricating oil in one another. It will be understood that the solubilizing agent may comprise any one of the compounds listed in Table II or mixtures thereof. Butane, isobutane, pentane and dimethyl ether are preferred. The amount of solubilizing agent is an amount effective to dissolve a sufficient amount of refrigerant in the lubricating oil such that the diluted oil can be transported back to the refrigeration compressor. Typically, the solubilizing agent is present in an amount of from about 0.1 to about 20 weight percent, preferably from about 0.1 to about 10 weight percent, more preferably from about 0.5 to about 5 weight percent, most preferably from about 1 to about 2.5 weight %, based on the total composition.

[0025] As used herein, the term lubricating oil refers to mineral or hydrocarbon oil; alkyl benzene oil; white or paraffinic oil; and mixtures thereof.. Suitable lubricating oils are commercially available from various sources (e.g., Capella brand names from Texaco and Suniso brand names from Sun Oil). The chemical compositions and uses of these oils are discussed in detail in the book "Fluorocarbon Refrigerants Handbook" by Ralph C. Downing, Prentice Hall, 1998, pp. 206-270. The amount of lubricating oil is an amount effective to provide acceptable lubrication to the compressor parts for its longevity. An effective amount of lubricating oil is the amount recommended by the equipment manufacturer. Typically, the lubricating oil is present in an amount of from about 1 to about 60 weight percent, more preferably from about 0.5 to about 5 weight percent, most preferably from about 1 to about 2.5 weight %, preferably from about 10 to about 50 based on the total composition.

Table I:

Refrigerants		
Refrigerant Number	Chemical Name	Chemical Formula
Methane Series		
11	Trichlorofluoromethane	CCl_3F

Table I: (continued)

Refrigerants		
Refrigerant Number	Chemical Name	Chemical Formula
Methane Series		
12	Dichlorodifluoromethane	CCl_2F_2
13	Chlorotrifluoromethane	$CClF_3$
14	Tetrafluoromethane (carbon tetrafluoride)	CF_4
21	Dichlorofluoromethane	$CHCl_2F$
22	Chlorodifluoromethane	$CHClF_2$
23	Trifluoromethane	CHF_3
30	Dichloromethane (methylene chloride)	CH_2Cl_2
31	Chlorofluoromethane	CH_2ClF
32	Difluoromethane (methylene fluoride)	CH_2F_2
40	Chloromethane (methylene fluoride)	CH_2F_2
41	Fluoromethane (methyl fluoride)	CH_3F
Ethane Series		
113	1,1,2-trichloro-1,2,2-trifluoroethane	CCl_2FCClF_2
114	1,2-dichloro-1,1,2,2-tetrafluoromethane	$CClF_2CClF_2$
115	Chloropentafluoroethane	$CClF_2CF_3$
116	Hexafluoroethane	CF_3CF_3
123	2,2-dichloro-1,1,1,-trifluoroethane	$CHCl_2CF_3$
124	1-chloro-1,1,1,2-tetrafluoroethane	$CHClFCF_3$
125	Pentafluoroethane	CHF_2CF_3
134a	1,1,1,2-tetrafluoroethane	CH_2FCF_3
141b	1,1-dichloro-1-fluoroethane	CH_3CCl_2F
142b	1-chloro-1,1-difluoroethane	CH_3CClF_2
143a	1,1,1-trifluoroethane	CH_3CF_3
152a	1,1-difluoroethane	CH_3CHF_2
Propane Series		
218	Octafluoropropane	CF3CF2CF3
227ea	1,1,1,2,3,3,3-heptafluoropropane	CF_3CHFCF_3
236fa	1,1,1,3,3,3-hexafluoropropane	$CF_3CH_2CF_3$
245fa	1,1,1-3,3-pentafluoropropane	$CF_3CH_2CHF_2$
Butane Series		
365	1,1,1,3,3-pentafluorobutane	$CF_3CH_2CF_2CH_3$
Cyclic Organic Compounds		
C318	Octafluorocyclobutane	$-(CF_2)_4-$

Table II:

Solubilizing Agents		
Refrigerant Number	Chemical Name	Chemical Formula
Miscellaneous Organic Compounds Hydrocarbons		
30	Dichloromethane (methylene chloride)	CH_2Cl_2
40	Chloromethane (methyl chloride)	CH_3Cl
50	Methane	CH_4
170	Ethane	CH_3CH_3
290	Propane	$CH_3CH_2CH_3$
600	Butane	$CH_3CH_2CH_2CH_3$
600a	Isobutane	$CH(CH_3)_2CH_3$
----	Pentane	$CH_3(CH_2)_3CH_3$
----	Isopentane	$CH_3CH(CH_3)CH_2CH_3$
----	Neopentane	$CH_3C(CH_3)_2CH_3$
----	Cyclopentane	$-(CH_2)_5-$
Fluorocarbons		
13I1	Iodotrifluoromethane	CF_3I
----	Pentafluorodimethyl ether	CF_2OCF_2H
152a	1,1-difluoroethane	CH_3CHF_2
161	Fluoroethane	CH_3CH_2F
218	Hexafluoroethane	CF_3CF_3
Oxygen compounds		
----	Dimethyl ether	CH_3OCH_3
610	Ethyl ether	$CH_3CH_2OCH_2CH_3$
----	Poly butylene glycols	$H-(O-CH_3CH_2CH_2CH_3)_n-OH$
611	Methyl formate	$HCOOCH_3$
Inorganic Compounds		
744	Carbon dioxide	CO_2
764	Sulfur hexafluoride	SF_6
Unsaturated Organic Compounds		
1150	Ethene (ethylene)	$CH_2=CH_2$
1270	Propene (propylene)	$CH_3CH=CH_2$

Table III:

Refrigerant Mixtures	
Refrigerant Number	Composition (Wt.%)
Zeotropes	
400	R-12/114 (40/60)
401A	R-22/152a/124 (53/13/34)

Table III: (continued)

Refrigerant Mixtures	
Refrigerant Number	Composition (Wt.%)
Zeotropes	
401B	R-22/152a/124 (61/11/28)
401C	R-22/152a/124 (33/15/52)
402A	R-125/290/22 (60/2/38)
402B	R-125/290/22 (38/2/60)
403A	R-290/22/218 (5/75/20)
403B	R-290/22/218 (5/56/39)
404A	R-125/143a/134a (44/52/4)
405A	R-22/152a/142b/C318 (45/7/5.5/42.5)
406A	R-22/600a/142b (55/4/41)
407A	R-32/125/134a (20/40/40)
407B	R-32/125/134a (10/70/20)
407C	R-32/125/134a (23/25/52)
407D	R-32/125/134a (15/15/70)
407E	R-32/125/134a (25/15/60)
408A	R-125/143a/22 (7/46/47)
409A	R-22/124/142b (60/25/15)
409B	R-22/124/142b (65/25/10)
410A	R-32/125 (50/50)
410B	R-32/125 (45/55)
411A	R-1270/22/152a) (1.5/87.5/11.0)
411B	R-1270/22/152a (3/94/3)
412A	R-22/218/143b (70/5/25)
413A	R-218/134a/600a (9/88/3)
414A	R-22/124/600a/142b (51/28.5/4/16.5)
414B	R-22/124/600a/142b (50/39/1.5/9.5)
Azeotropes	
500	R-12/152a (73.8/26.2)
501	R-22/12 (75.0/25.0)
502	R-22/115 (48.8/51.2)
503	R-23/13 (40.1/59.9)
504	R-32/115 (48.2/51.8)
505	R-12/31 (78.0/22.0)
506	R-31/114 (55.1/44.9)
507A	R-125/143a (50/50)
508A	R-23/116 (39/61)
508B	R-23/116 (46/54)

Table III: (continued)

Refrigerant Mixtures	
Refrigerant Number	Composition (Wt.%)
Azeotropes	
509A	R-22/218 (44/56)

Table IV:

Hydrofluorocarbon Refrigerant Mixtures				
Mixture #	R-32 wt.%	R-125 wt.%	R-143a wt.%	R-134a wt.%
1	10 to 80	90 to 20	-	-
2	5 to 45	5 to 45	-	90 to 10
3	-	30 to 90	70 to 10	-
4	-	60 to 40	39 to 20	2 to 40

[0026] The components of the composition of the invention are known materials that are commercially available or may be prepared by known methods. Preferably, the components are of sufficiently high purity so as to avoid the introduction of adverse influences on the properties of the system.

[0027] The compositions of the invention may also contain additives such as oxidation resistance and thermal stability enhancers, corrosion inhibitors, metal deactivators, lubricity additives, viscosity index enhancers, pour and/or floc point depressants, detergents, dispersants, antifoaming agents, anti-wear agents, and extreme pressure resistant additives. Many additives are multifunctional. For example, certain additives may impart both anti-wear and extreme pressure resistance properties, or function both as a metal deactivator and a corrosion inhibitor. Cumulatively, all additives preferably do not exceed 8% by weight, or more preferably do not exceed 5% by weight, of the total composition.

[0028] An effective amount of the foregoing additive types is generally in the range from 0.01 to 5% for the antioxidant component, 0.01 to 5% for the corrosion inhibitor component, from 0.001 to 0.5% for the metal deactivator component, from 0.5 to 5% for the lubricity additives, from 0.01 to 2% for each of the viscosity index enhancers and pour and/or floc point depressants, from 0.1 to 5% for each of the detergents and dispersants, from 0.001 to 0.1% for anti-foam agents, and from 0.1-2% for each of the anti-wear and extreme pressure resistance components. All these percentages are by weight and are based on the total composition. It is to be understood that more or less than the stated amounts of additives may be more suitable to particular circumstances, and that a single molecular type or a mixture of types may be used for each type of additive component. Also, the examples listed below are intended to be merely illustrative and not limiting.

[0029] Examples of suitable oxidation resistance and thermal stability enhancers are diphenyl-, dinaphthyl-, and phenylnaphthyl-amines, in which the phenyl and naphthyl groups can be substituted, e.g., N,N'-diphenyl phenylenediamine, p-octyldiphenylamine, p,p-dioctyldiphenylamine, N-phenyl-1-naphthyl amine, N-phenyl-2-naphthyl amine, N-(p-dodecyl)phenyl-2-naphthyl amine, di-1-naphthylamine, and di-2-naphthylamine; phenothazines such as N-alkylphenothiazines; imino(bisbenzyl); and hindered phenols such as 6-(t-butyl) phenol, 2,6-di-(t-butyl) phenol, 4-methyl-2,6-di-(t-butyl) phenol, 4,4'-methylenebis(2,6-di-{t-butyl} phenol), and the like.

[0030] Examples of suitable cuprous metal deactivators are imidazole, benzamidazole, 2-mercaptobenzthiazole, 2,5-dimercaptothiadiazole, salicylidine-propylenediamine, pyrazole, benzotriazole, tolutriazole, 2-methylbenzamidazole, 3,5-imethyl pyrazole, and methylene bis-benzotriazole. Benzotriazole derivatives are preferred. Other examples of more general metal deactivators and/or corrosion inhibitors include organic acids and their esters, metal salts, and anhydrides, e.g., N-oleyl-sarcosine, sorbitan mono-oleate, lead naphthenate, dodecenyl-succinic acid and its partial esters and amides, and 4-nonylphenoxy acetic acid; primary, secondary, and tertiary aliphatic and cycloaliphatic amines and amine salts of organic and inorganic acids, e.g., oil-soluble alkylammonium carboxylates; heterocyclic nitrogen containing compounds, e.g., thiadiazoles, substituted imidazolines, and oxazolines; quinolines, quinones, and anthraquinones; propyl gallate; barium dinonyl naphthalene sulfonate; ester and amide derivatives of alkenyl succinic anhydrides or acids, dithiocarbamates, dithiophosphates; amine salts of alkyl acid phosphates and their derivatives.

[0031] Examples of suitable lubricity additives include long chain derivatives of fatty acids and natural oils, such as esters, amines, amides, imidazolines, and borates.

[0032] Examples of suitable viscosity index enhancers include polymethacrylates, copolymers of vinyl pyrrolidone and methacrylates, polybutenes, and styrene-acrylate copolymers.

[0033] Examples of suitable pour point and/or floc point depressants include polymethacrylates such as methacrylate-ethylene-vinyl acetate terpolymers; alkylated naphthalene derivatives; and products of Friedel-Crafts catalyzed condensation of urea with naphthalene or phenols.

[0034] Examples of suitable detergents and/or dispersants include polybutenylsuccinic acid amides; polybutenyl phosphonic acid derivatives; long chain alkyl substituted aromatic sulfonic acids and their salts; and metal salts of alkyl sulfides, of alkyl phenols, and of condensation products of alkyl phenols and aldehydes.

[0035] Examples of suitable anti-foam agents include silicone polymers and some acrylates.

[0036] Examples of suitable anti-wear and extreme pressure resistance agents include sulfurized fatty acids and fatty acid esters, such as sulfurized octyl tallate; sulfurized terpenes; sulfurized olefins; organopolysulfides; organo phosphorus derivatives including amine phosphates, alkyl acid phosphates, dialkyl phosphates, aminedithiophosphates, trialkyl and triaryl phosphorothionates, trialkyl and triaryl phosphines, and dialkylphosphites, e.g., amine salts of phosphoric acid monohexyl ester, amine salts of dinonylnaphthalene sulfonate, triphenyl phosphate, trinaphthyl phosphate, diphenyl cresyl and dicresyl phenyl phosphates, naphthyl diphenyl phosphate, triphenylphosphorothionate; dithiocarbamates, such as an antimony dialkyl dithiocarbamate; chlorinated and/or fluorinated hydrocarbons, and xanthates.

Examples

Example 1

[0037] Critical flammability ratio (CFR) of mixtures determined using Underwriter Laboratories Refrigerant Flammability test method 2182. CFR allows determination of what level of flammable material can be incorporated, without the mixture itself becoming flammable. Butane and dimethyl ether (DME) were added to R-407C (23 wt.% R-32; 25 wt.% R-125 and 52 wt.% R-134a) as the flammable additive.

Temp. (°C)	Additive	Wt.%
25	Butane	3.4
60	Butane	3.1
100	Butane	2.5
25	DME	3.3
60	DME	2.7
100	DME	2.1

[0038] The table indicates that certain 32/125/134a/butane (or DME) compositions are nonflammable per the widely used refrigerant flammability method.

Example 2

[0039] Actual testing in a refrigeration machine of a composition of the invention (test mixture: 22.5 wt.% R-32, 24.5 wt.% R-125, 51 wt.% R-134a, 2 wt.% butane) was performed under typical air conditioning conditions and using mineral oil supplied by the compressor manufacturer (Copeland blended white oil Catalog No. 999-5170-31).

[0040] Testing was performed in a 2 ton air conditioner system setup similar to the unit reported in Report DOE/CE/23810-71 "Study of Lubricant Circulation in HVAC Systems," March 1995-April 1996 (author Frank R. Biancardi et. al.; prepared for Air Conditioning and Refrigeration Technology Institute Under ARTI/MCLR Project No. 665-53100) except that instead of equal size risers, three different size risers (3/4", 7/8" and 11/8") were used to allow a greater variety of velocities. Also the ability to pump oil from the compressor sump into the compressor discharge line was added. Using a hand pump, 90cc of oil from the sump was injected into the compressor discharge line. By observing the oil level in the compressor sump versus time, the rate and time required for oil return was measured.

Composition	Capacity (tons)	COP	Oil return rate (cc/min)	Completion Time (min)
R-407C	1.70	2.9	2.4	65
Test Mixture	1.88	3.3	2.7	46

[0041] Oil return is important for compressor reliability purposes. The example demonstrates that both capacity and efficiency of the system are enhanced over R-407C in the absence of the solubilizing agent and the oil return is improved as well (in mineral oil systems).

Examples 3-7

[0042] The performance of mixtures of HFC refrigerant R-407C is obtained in the presence and absence of solublizing agents in a thermodynamic refrigeration cycle operating in typical air conditioning application (100°F condensing temperature and 40°F evaporating temperature). The vapor pressure of each mixture is measured at 25°C.

Ex. No.	32/125/134a Refrigerant Mixture (wt.%)	Solubilizing Agent	Wt.%	Refrigeration Capacity relative to R-407C	Vapor Pressure relative to R-407C (25°C)	Oil Return
3	23/25/52 (R-407C)	--	0	1	1	No
4	21.9/23.8/49.3	Propane	5	1.05	1.05	Yes
5	21.9/23.8/49.3	Butane	5	1.00	0.99	Yes
6	22.6/24.5/51.0	Butane	2	1.00	1.00	Yes
7	20.9/22.7/47.4	Butane	10	1.00	0.98	Yes

[0043] Example 3 demonstrates that the HFC itself is unsuitable for use with hydrocarbon oil in that without oil return the compressor may be damaged.

[0044] Example 4 demonstrates that although there is oil return, the addition of propane results in an undesirable increase in the pressure of the system.

[0045] Examples 5-7 demonstrate that the use of butane results in oil return without an undesirable pressure increase. This is particularly important for retrofitting applications.

Claims

1. A composition comprising:

   (i) a hydrofluorocarbon refrigerant; and
   (ii) a solubilizing agent selected from the group consisting of butane, isobutane, pentane, dimethyl ether and mixtures thereof.

2. The composition of claim 1 wherein the hydrofluorocarbon refrigerant comprises a compound selected from the group consisting of R-32, R-125, R-134a, R-143a and mixtures thereof.

3. The composition of claim 1 wherein the hydrofluorocarbon refrigerant is a mixture of R-32, R-125 and R-134a.

4. The composition of claim 1 wherein the hydrofluorocarbon refrigerant is a mixture of R-32 and R-125.

5. The composition of claim 1 wherein the hydrofluorocarbon refrigerant is a mixture of R-143a, R-125 and R-134a.

6. The composition of claim 1 wherein the hydrofluorocarbon refrigerant is a mixture of R-125 and R-143a.

7. The composition of claim 1 wherein the hydrofluorocarbon refrigerant is selected from the group consisting of the compositions listed in Table III.

8. The composition of claim 1 wherein the hydrofluorocarbon refrigerant is selected from the group consisting of R-404A, R-407C, R-410A and R-507A.

9. The composition of claim 1 wherein the hydrofluorocarbon refrigerant is selected from the group consisting of the compositions listed in Table IV.

10. The composition of any one of claims 1-9 wherein the solubilizing agent is butane.

11. The composition of any one of claims 1-9 wherein the solubilizing agent is isobutane.

12. The composition of claim 1 which comprises about 80-99.9 weight percent of R407C and about 0.1-10 weight percent of butane.

13. The composition of claim 1 which comprises about 80-99.9 weight percent of R410A and about 0.1-10 weight percent of butane.

14. The composition of any one of claims 1-9 wherein the solubilizing agent is pentane.

15. The composition of any one of claims 1-9 wherein the solubilizing agent is dimethyl ether.

16. The composition of any preceding claim further comprising a lubricating oil selected from the group consisting of mineral or hydrocarbon oil, alkyl benzene oil, white or paraffinic oil and mixtures thereof.

17. A method for producing refrigeration which comprises condensing a composition as defined in any of claims 1 to 15 and thereafter evaporating the composition in the vicinity of a body to be cooled.

18. A method for producing heating which comprises condensing a composition as defined in any of claims 1 to 15 in the vicinity of a body to be heated and thereafter evaporating the composition.

19. A method of recharging a refrigeration system of the type containing a chlorine-containing refrigerant and a lubricating oil, comprising the steps of:

(a) removing said chlorine-containing refrigerant from said refrigeration system while leaving substantially all of said lubricating oil in said system; and
(b) introducing to said lubricating oil left in said system a composition as defined in any of claims 1 to 15.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 31 0474

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 1 018 538 A (NIPPON MITSUBISHI OIL CORP) 12 July 2000 (2000-07-12) * paragraph [0008] - paragraph [0009] * * paragraph [0102] - paragraph [0106]; tables 6,7 *	1-13, 16-18	C09K5/04
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A	US 4 364 236 A (LOWER RALPH C ET AL) 21 December 1982 (1982-12-21) * the whole document *	19	

A	US 4 862 699 A (LOUNIS SAID) 5 September 1989 (1989-09-05) * the whole document *	19	

X	WO 96 03473 A (MURPHY FREDERICK THOMAS ;CORR STUART (GB); ICI PLC (GB); MORRISON) 8 February 1996 (1996-02-08) * page 3, line 5 - page 5, line 23; claims 1-21; examples 1-12; tables 1-8 *	1-9,14, 16-18	
A	---	19	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
X	EP 0 659 862 A (SANYO ELECTRIC CO) 28 June 1995 (1995-06-28) * column 5, line 18 - column 8, line 38; claims 1-8 *	1-3,7-9, 14,16-18	C09K C10M
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X	GB 2 274 463 A (ICI PLC) 27 July 1994 (1994-07-27) * page 6, line 32 - page 8, line 28; claims 1-3 *	1-9, 15-18	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	23 May 2001	olde Scheper, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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EPO FORM 1503 03.82 (P04C01)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 31 0474

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 638 623 A (AUSIMONT SPA) 15 February 1995 (1995-02-15) * claims 1,3; examples 6-8; table 1 * ---	1-9, 15-18	
X	EP 0 598 907 A (DAIKIN IND LTD) 1 June 1994 (1994-06-01) * page 3, line 54; claims 1-7 * -----	1,2,6-9, 15-18	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	23 May 2001	olde Scheper, B

CATEGORY OF CITED DOCUMENTS

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EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 31 0474

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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23-05-2001

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EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

DERWENT-ACC-NO: 2002-464721

DERWENT-WEEK: 200250

TITLE: Refrigerant composition, e.g. for refrigeration, air conditioning and heat pump applications, comprises hydrofluorocarbon refrigerant and solubilizing agent

INVENTOR: RICHARD R G; SINGH R R ; THOMAS R H P ; WILSON D P

PATENT-ASSIGNEE: HONEYWELL INT INC[HONE]

PRIORITY-DATA: 2000US-670738 (September 27, 2000)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE
EP 1193305 A1	April 3, 2002	EN

DESIGNATED-STATES: AL AT BE CH CY DE DK ES FI FR GB GR IE IT LI LT LU LV MC MK NL PT RO SE SI TR

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
EP 1193305A1	N/A	2000EP-310474	November 24, 2000

INT-CL-CURRENT:

TYPE	IPC DATE
CIPS	C09K5/04 20060101
CIPS	C10M171/00 20060101

RELATED-ACC-NO: 2002-463198 2004-282574

ABSTRACTED-PUB-NO: EP 1193305 A1

BASIC-ABSTRACT:

NOVELTY - Refrigerant composition comprises a hydrofluorocarbon refrigerant; and a solubilizing agent including butane, isobutane, pentane, dimethyl ether, or their mixtures.

DESCRIPTION - INDEPENDENT CLAIMS are also included for;

(1) A method for producing refrigeration, which involves condensing the above composition, and evaporating the composition in the vicinity of a body to be cooled;

(2) A method for producing heating, which involves condensing the inventive composition in the vicinity of a body to be heated, and evaporating the composition; and

(3) A method of recharging a refrigeration system of the type containing a chlorine-containing refrigerant and a lubricating oil, which involves removing the chlorine-containing refrigerant from the refrigeration system while leaving all of the lubricating oil in the system, and introducing to the lubricating oil left in the system the inventive composition.

USE - The refrigerant composition is used in industry for refrigeration, air conditioning, and heat pump applications. It is used as refrigerants, aerosol propellants, heat transfer media, gaseous dielectrics, fire-extinguishing agents, foam blowing agents, and solvents. It is used as R-22 retrofit fluids.

ADVANTAGE - The inventive refrigerant composition is soluble in hydrocarbon oil, thus allowing for a simpler and less expensive retrofit option to the refrigerant user.

EQUIVALENT-ABSTRACTS:

ORGANIC CHEMISTRY

Preferred Components: The hydrofluorocarbon refrigerant comprises a compound including R-32, R-125, R-134a, R-143a, or their mixtures. It can be one of the compositions listed in Table III and IV as disclosed. It includes R-404A, R-407C, R-410A, or R-507A. The solubilizing agent is butane or isobutane. It can be pentane or dimethyl ether. The composition further comprises a lubricating oil including mineral or hydrocarbon oil, alkyl benzene oil, white or paraffinic oil, or their mixtures.

Preferred Composition: The composition comprises 80-99.9 wt.% R407C or R410A and 0.1-10 wt.% butane.

Actual testing in a refrigeration machine of the inventive composition comprising 22.5 wt.% R-32, 24.5 wt.% R-125, 51 wt.% R-134a, and 2 wt.% butane was performed. Testing was performed in a 2 ton air conditioner system setup similar to the unit reported in Report DOE/CE/23810-71 Study of Lubricant Circulation in HvAC Systems, March 1995-April 1996 (author Frank R. Biancardi et. al., prepared for Air Conditioning and Refrigeration Technology Institute Under ARTI/MCLR Project No. 665-53100 except that instead of equal size risers, three different size risers (3/4, 7/8, and 11/8) were used. Using a hand pump, 90

cc of oil from the sump was injected into the compressor discharge line. The rate and time required for oil return was respectively measured to be 2.7 cc/min and 46 minutes for the test mixture, and 2.4 cc/min and 65 minutes for R-407C, demonstrating that both capacity and efficiency of the system were enhanced over R-407C and the oil return was improved.

TITLE-TERMS: REFRIGERATE COMPOSITION AIR CONDITION HEAT PUMP APPLY COMPRISE SOLUBLE AGENT

DERWENT-CLASS: B07 D21 E19 G04 H07 H08 J07 K01 L03 X27

CPI-CODES: B04-B01C3; B10-H01; B10-H02B; B10-J02; B11-C09; D08-B10; E10-H01E; E10-H04A3; E10-J02D2; E10-J02D3; G04-B01; H07-X; H08-D09; J07-A08; K01-A; L03-D01;

EPI-CODES: X27-F;

CHEMICAL-CODES: Chemical Indexing M1 *01* Fragmentation Code M210 M211 M212 M213 M214 M215 M216 M220 M221 M222 M223 M224 M225 M226 M231 M232 M233 M320 M416 M423 M430 M610 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds RA00NG Registry Numbers 103243

Chemical Indexing M2 *02* Fragmentation Code M210 M214 M231 M320 M416 M430 M610 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds R00804 Registry Numbers 8441

Chemical Indexing M2 *03* Fragmentation Code M210 M214 M232 M320 M416 M430 M610 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds R00355 Registry Numbers 2973

Chemical Indexing M2 *04* Fragmentation Code M210 M215 M231 M320 M416 M430 M610 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds R00879 Registry Numbers 41

Chemical Indexing M2 *05* Fragmentation Code H5 H581 H8 M210 M211 M272 M282 M320 M416 M430 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds R00965 Registry Numbers 383

Chemical Indexing M2 *06* Fragmentation Code H6 H601 H608 H684 H685 M280 M312 M321 M332 M344 M363 M391 M416 M430 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds R16771 Registry Numbers 133559

Chemical Indexing M2 *07* Fragmentation Code H6 H601 H681 H685 M280 M312 M321 M332 M344 M363 M391 M416 M430 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds R16596 Registry Numbers 11573

Chemical Indexing M2 *08* Fragmentation Code H6 H685 M280 M312 M321 M331 M343 M363 M391 M416 M430 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds R11342 Registry Numbers 11569

Chemical Indexing M3 *02* Fragmentation Code M210 M214 M231 M320 M416 M430 M610 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds R00804 Registry Numbers 8441

Chemical Indexing M3 *03* Fragmentation Code M210 M214 M232 M320 M416 M430 M610 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds R00355 Registry Numbers 2973

Chemical Indexing M3 *04* Fragmentation Code M210 M215 M231 M320 M416 M430 M610 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds R00879 Registry Numbers 41

Chemical Indexing M3 *05* Fragmentation Code H5 H581 H8 M210 M211 M272 M282 M320 M416 M430 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds R00965 Registry Numbers 383

Chemical Indexing M3 *06* Fragmentation Code H6 H601 H608 H684 H685 M280 M312 M321 M332 M344 M363 M391 M416 M430 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds R16771 Registry Numbers 133559

Chemical Indexing M3 *07* Fragmentation Code H6 H601 H681 H685 M280 M312 M321 M332 M344 M363 M391 M416 M430 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds R16596 Registry Numbers 11573

Chemical Indexing M3 *08* Fragmentation Code H6 H685 M280 M312 M321 M331 M343 M363 M391 M416 M430 M620 M782 Q140 Q337 Q432 Q433 Q434 Q435 Specific Compounds R11342 Registry Numbers 11569

Chemical Indexing M6 *09* Fragmentation Code Q140 Q254 Q337 Q432 Q433 Q434 Q435 R524

UNLINKED-DERWENT-REGISTRY-NUMBERS: ; 0355U ; 0804U ; 0879U ; 1781U

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: 2002-132346